

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
3 July 2003 (03.07.2003)

PCT

(10) International Publication Number
WO 03/054091 A1

(51) International Patent Classification⁷: **C09D 11/10, C08F 222/10**

(74) Agents: **BARUH, Colette et al.; UCB, S.A., Intellectual Property Department, 60, Allée de la Recherche, B-1070 Bruxelles (BE).**

(21) International Application Number: **PCT/EP02/14544**

(81) Designated States (national): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) International Filing Date:
19 December 2002 (19.12.2002)

(84) Designated States (regional): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(25) Filing Language: **English**

(26) Publication Language: **English**

(30) Priority Data:
01130747.7 20 December 2001 (20.12.2001) EP

(71) Applicant (for all designated States except US): **UCB, S.A. [BE/BE]; 60, Allée de la Recherche, B-1070 Bruxelles (BE).**

Published:

- *with international search report*
- *before the expiration of the time limit for amending the claims and to be republished in the event of receipt of amendments*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(72) Inventors; and

(75) Inventors/Applicants (for US only): **BERGIERS, Francis [BE/BE]; 35, rue de la Mazerine, B-1310 La Hulpe (BE). BHATTACHARYA, Indrajit [IN/IN]; 201 Mahdu Park, 155 Sher-e-Punjab Society, Andheri East, 400 093 Mumbai (IN). LINDEKENS, Luc [BE/BE]; 126, Dooren, B-1785 Merchtem (BE). VAN DEN BRANDEN, Stefan [BE/BE]; 59, Nieuwstraat, B-2550 Kontich (BE).**



WO 03/054091 A1

(54) Title: RADIATION CURABLE COMPOSITIONS FOR PIGMENTED LIQUID INKS

(57) Abstract: The invention concerns radiation curable liquid pigmented ink composition, wherein ticyclodecyl di(meth)acrylate and/or tricyclodecyl mono(meth)acrylate are particularly good wetting agent. The compositions are used in ink jet inks, gravure inks and flexographic inks.

Radiation curable compositions for pigmented liquid inks.

The invention relates to radiation curable compositions containing essentially tricyclodecyl di(meth)acrylate or tricyclodecyl mono(meth)acrylate, used as pigmented 5 liquid inks. Liquid inks comprise flexographic inks, gravure inks and more particularly ink jet inks.

In ink jet printing, small drops of ink are projected directly onto an ink receptor surface without physical contact between the printer and the substrate. The printing 10 device stores the printing data electronically and controls a mechanism for ejecting the drops image-wise. This can be performed in several different ways. In continuous ink jet printing, the drops are continuously generated and are charged electrostatically and deflected to be printed or to be recollected. In drop on demand (DOD) printing, drops are 15 only ejected when they are used in imaging. The droplets can be formed by means of pressure created by a piezoelectric transducer or by thermal pushes via the formation of a bubble.

Ink compositions for ink jet include dye or pigment, water or solvent (not in UV and hot melt inks), polymeric binder, humectant and additives such as photoinitiator in 20 radiation curable inks, preservatives, dispersing agents. Inks can be divided in different types. In water based inks, drying involves absorption and penetration into the substrate, followed by evaporation. In oil based types of inks, drying involves absorption and 25 penetration. In solvent based inks, the drying involves mostly evaporation of the solvent. Hot melt inks are solid at room temperature, but ejected in molten state. Finally, the radiation curable inks dry by polymerization.

Systems based on water and solvents suffer from a number of drawbacks. Volatile 30 organic compounds (VOC) must be evaporated. Their drying is slow, more rapid for solvent based inks than for water based ones. Their use is limited to porous substrates. Frequently, blocking of the printing head nozzles occurs due to drying of the ink. The viscosity changes due to evaporation in the head. Finally, the prints have poor chemical resistance.

Radiation curable inks do not exhibit these disadvantages, but other problems 35 arise in these inks. The difficulty lays in the combination of a series of properties. Each property independently can be solved, but for the total set of properties, compromises have to be made.

CONFIRMATION COPY

One of these properties that the inks must present is a very low viscosity, in the range of 5 to 25 mPa.s, for example 15 mPa.s at printing temperature, in order to be jettable in small droplets of a volume in the picoliter range. To reach these low viscosity 5 values, radiation curable inks must contain very high levels of reactive diluent. But these reactive diluents having low viscosity also have a low radiation curing reactivity and generally have a bad smell, which can be accompanied with irritation problems.

Another important problem is the pigment wetting properties of the reactive diluents. In contrast to inks based on dyes, which are soluble, pigments are solids and 10 have to be dispersed in the ink. Pigmented inks offer better light fastness but lead to higher viscosity. If the pigment wetting properties of a diluent are good, the viscosity of the ink will be lower than inks based on poor pigment wetters, if the starting viscosity of the pure, unpigmented diluent is the same. Also, inks made with products having poor 15 pigment wetting properties show a low stability in time, which results in the flocculation or the precipitation of the pigment. Also, good wetting properties of the products reduce the number of passes needed in the grinding process in a bead mill required to bring the particle size to a submicron level. This brings about a reduction in time and in labor consuming step. Finally, good wetting properties permit to increase the pigment load of the ink, which brings about a higher color strength or a decrease of the print thickness 20 still keeping the same color strength. Better pigment wetting also results in a better transparency of the printed ink layer.

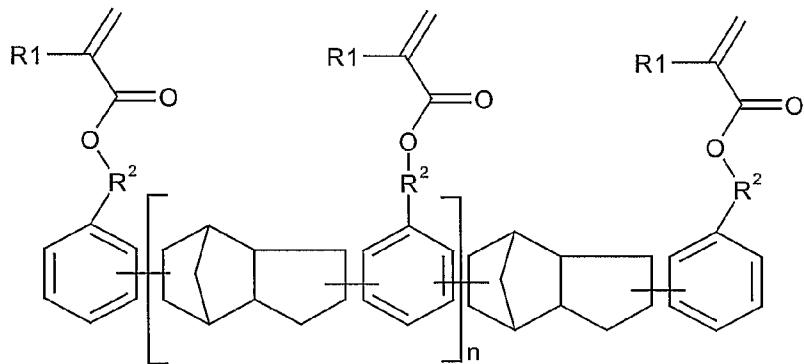
The same principles are valid for other liquid ink technologies, gravure and flexo(graphic) printing, although to a lesser extent. Indeed, in gravure printing the image and text are engraved in a metal roller in form of 25 cells. These engraved cells must be filled by a liquid ink of about 100 mPa.s. The excess of ink is squeezed away by a metal doctor blade. The ink is then transferred on the substrate (paper, aluminum foil or polymer films) by capillarity.

Flexography printing is a process where the image, which is formed on a soft rubber plate, receives a liquid ink from a special fully engraved ceramic roller, called 30 anilox. The viscosity of the inks must be in the range of from 400 to 1000mPa.s. The ink is then transferred on the substrate.

As can be seen from the viscosity used in these printing processes the pigment wetting-viscosity relationship is less critical but still very challenging. The viscosity range of the UV-inks range from approximately 20 mPa.s for ink jet over 100 mPa.s for gravure 35 to 1000 mPa.s for flexographic printing.

Within the following specification, a liquid ink is defined as an ink whose viscosity, measured at a temperature of 25°C and at a shear rate of 500 s⁻¹, is at most 1000 mPa.s.

Many publications exist concerning printing technologies such as offset printing or serigraphy, the latter being used for example to apply photoresist ink compositions. Such 5 technologies require ink compositions exhibiting high viscosity, typically at least 20000mPa.s for offset printing. For example, JP 57-164163 discloses offset printing inks compositions containing (meth)acrylate derivative of tricyclodecane dimethylool as adhesion enhancer/greasing effect dereaser. JP 08311130 shows a photoresist composition containing (A) a vinyl ester resin having the general formula:



10

wherein R1 and R2 expresses a H or a methyl group and n is 0 or 1.
and (B) tricyclodecanedimethylool diacrylate.

Many publications have already been made on liquid radiation curable ink compositions. For example, EP 0 540 203 discloses VOC free UV inkjet compositions containing up to 70 % monofunctional or difunctional acrylates. WO 97/31071 describes 15 radiation curable inkjet composition comprising low viscous and low toxic alkoxyolated oligomers in a range from 80 to 95 %. EP 0 997 507 is concerned by radiation curable inkjet ink compositions containing at least 30 % of an amine functionalised polyether acrylate for increased cure speed. WO 99/29787 discloses a radiation curable ink jet ink 20 of low viscosity and comprising a colorant, a reactive liquid material formed of both monofunctional and polyfunctional material and 5 to 30% by weight of at least one oligomer.

The present invention offers a much better compromise of properties required for liquid inks, than what is actually available. A very good pigment wetting is obtained 25 resulting in a combination of low viscosity, good flow and good color strength. The formulated pigment paste is easier to grind and less energy and time are thus required to obtain sufficiently small particles. This results in a more economical grinding process.

The stability of the ink is increased, which results in less settling of the pigment and less risk of clogging in the printing head. Furthermore the ink shows good reactivity and a low odor. These results are obtained through the use of tricyclodecyl di(meth)acrylate and/or tricyclodecyl mono(meth)acrylate as a constituent of the liquid ink.

5. This is why the present invention is concerned by a radiation curable liquid ink composition which comprises tricyclodecyl di(meth)acrylate and/or tricyclodecyl mono(meth)acrylate and a pigment.

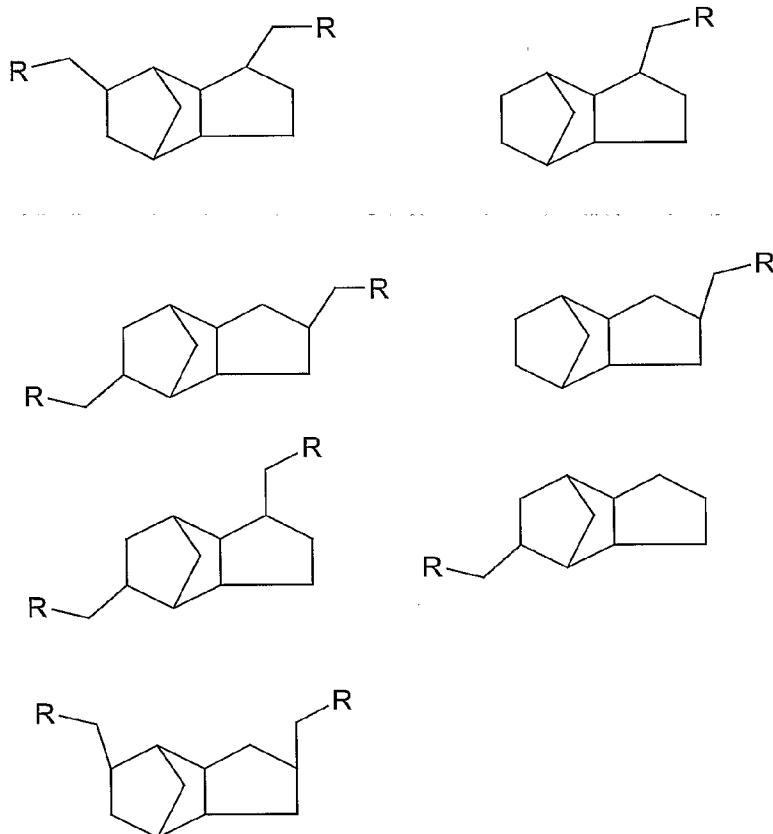
It has been observed that tricyclodecyl di(meth)acrylate and/or tricyclodecyl mono(meth)acrylate permit to provide liquid ink compositions exhibiting together low 10 viscosity and good pigment wetting, as demonstrated in the foregoing examples by various methods comprising a low value of the shortness index (SI).

More particularly, the radiation curable ink composition comprises:

- (a) 1-85% by weight of tricyclodecyl di(meth)acrylate and/or tricyclodecyl mono(meth)acrylate;
- 15 (b) 1-50% by weight of a pigment;
- (c) 0-85% by weight of an acrylic and/or methacrylic derivative;
- (d) 0-15% by weight of a dispersing agent;
- (e) 0-10% by weight of additives,
- (f) 0-15% by weight of photoinitiators

20 calculated on the total weight of the composition.

The tricyclodecyl di(meth)acrylate and/or mono(meth)acrylate referred to in this specification are in fact a mixture of isomers which may be represented by the formulas:



R = acrylate, methacrylate

Difunctional monomers are called 2-propenoic acid, [octahydro-4,7-methano-1H-indene-1,5(or 1,6 or 2,5 or 2,6)-diyl] bis(methylene) ester, as far as the acrylated monomers are concerned. The acrylated monofunctional monomers are called 2-propenoic acid, [octahydro-4,7-methano-1H-inden-1(or 2 or 5)-yl]methyl ester. The methacrylated corresponding compounds are called 2-methyl-2-propenoic acid, followed by the same name as the acrylated compounds. The acrylated mixture of tricyclodecyl dimethanol(s) is commercially available from Nippon Kayaku under the trademark Kayarad DCP-A and Kayarad R684, from Toagosei Chemical Industry under the trademark Aronix M203 and from Mitsubishi Chemicals under the trademark Yupimer UV-SA 1002. Tricyclodecyl diacrylate is in the further text often abbreviated as TCDA.

This diluent may be used at 1-85% by weight on the total weight of the ink, but it is preferably used at 10-50 % by weight.

The pigments used according to the invention are every pigments used in liquid inks. A list of such pigments can be found in the Colour Index. More particularly, those

pigments may be cited such as Process Yellow 13 (Diarylide Yellow - Irgalite BAW of Ciba, Permanent GR of Clariant), Process Magenta Pigment 57 (Bona Calcium - Illobona 4BY of Sun , Irgalite SMA of Ciba), Process Blue 15.3 (Copper Phthalocyanine - Irgalite GLO of Ciba, Hostaperm Blue B2G of Clariant), Process Black 7 (Oxidised Carbon Black - Special Black 250; Special Black 350 of Degussa), etc. The pigments are used at 1-50% by weight of the total weight of the composition, preferably at 1-40 % by weight.

The acrylic or methacrylic derivatives used according to the invention are those currently used in radiation curable compositions, especially in the ink field. These can be chosen among mono- di- and tri acrylates like isobornyl acrylate, phenoxyethyl acrylate, tetrahydrofurfuryl acrylate, dipropylene glycol diacrylate, tripropylene glycol diacrylate, hexanediol diacrylate, trimethylolpropane triacrylate or alkoxyLATED acrylates like propoxylated neopentylglycol diacrylate, oxyethylated trimethylolpropane triacrylate, oxypropylated glycerol triacrylate. Oligomers may also be used, such as amino (meth)acrylates, polyester (meth)acrylates, urethane (meth)acrylates, epoxy (meth)acrylates, etc. An alkoxyLATED acrylate bisphenol A-derivative, for example the one sold by UCB, S.A. under the tradename Ebecryl 150, can be used.

AlkoxyLATED (meth)acrylate compounds are preferred as they are less irritant than their non alkoxyLATED countertypes.

These acrylic or methacrylic derivatives are used at 0-85% by weight of the total weight of the composition, preferably at 10-60 % by weight.

The photoinitiators usable in the ink compositions of the invention are well known in the art. They can be chosen from α -hydroxyketones, α -aminoketones, benzildimethyl-ketals, acyl phosphines, benzophenone derivatives, thioxanthones and blends of these. They are used at 0 to 15% by weight. Photoactivators are chosen between amine derivatives. The photoinitiators need only be used if the compositions are cured by ultraviolet light. The compositions may also be cured by electron beams rays, and, in this case, no photoinitiator needs to be added to the composition.

The dispersing agents are classic, such as Disperbyk, EFKA, Solsperse, Ser-Ad etc.

The additives are those commonly used in inks, such as stabilizers, substrate wetting agents, anti-foam agents, adhesion promoters, etc.

Inks are generally made in 2 steps, the pigment dispersion step and the letdown step. In the 1st step, all the pigments are added in the pigment dispersing binders (oligomers and monomers). They are mixed and then dispersed on a triple roll or bead mill. A few passes are necessary to achieve a good dispersion. Pigments that are difficult to disperse require more number of passes. It is the same with the binders. Binders that

are not good for pigment wetting also require additional passes. Once the pigment has achieved this fineness, the pigment paste is diluted with the letdown. The letdown has to be compatible with the binder used to disperse the pigments. The finished ink is then printed onto the substrate. The ink film is then cured under a UV lamp, for example at 5 120W/cm and 30 m/min. A few passes may be required to cure the ink if the binder is not reactive enough.

The invention also relates to the polymeric compositions obtained or obtainable by curing the radiation curable liquid ink composition.

Examples.

10 Pigment wetting can be evaluated by different methods:

- For liquid inks a Newtonian rheology is required. Ideally, this means that the viscosity is independent of the shear rate. Pigment wetting is a major factor of influence on the rheology. Inks with bad wetting of the pigment are showing a marked shear thinning effect, whereby the viscosity is high at low shear rate and drops as the shear rate is increased. The rheology is measured with cone and plate type rheometers.
- Pigment wetting can also be evaluated by measuring the color density of the printed ink at constant film thickness. In this case the ink is printed using a lab applicator and the color density is measured with a densitometer, which spectrophotometrically compares the reflected light to the incident light.
- A third way to evaluate pigment wetting is to look at the transparency of the printed ink layer. In this test the clarity of a pattern below the printed ink is visually evaluated. The better the clarity, the better the pigment wetting.
- Finally the pigment wetting characteristics can also be followed by microscopic evaluation. Flocculation or aggregation of pigment particles can be seen under the microscope in diluted inks.

Practically, a series of monomers were evaluated with four pigments (Cyan, Magenta, Yellow and Black). The properties tested were:

30

- Rheology and flow, which were measured on the liquid ink, with an apparatus Physica UDS200 (Paar-Physica), which is a plate and cone viscometer. The measurement geometry was of a diameter of 50 mm and an angle of 2° for the cone. The measurement was a flow curve in controlled shear rate ranging from $D = 0,1 \text{ s}^{-1}$ to $D = 500 \text{ s}^{-1}$ at 25 °C.

- Transparency and gloss were evaluated on the printed concentrated and diluted ink with the naked eye.
- The printed inks were also inspected by microscopy for pigment flocculation or aggregation.

5 Example 1. Preparation of the ink compositions

Inks are prepared according to above-mentioned process. In the pigment dispersion step, all the pigments are added in the pigment dispersing binders (oligomers and monomers). They are mixed manually with knife and then dispersed on a triple roll or bead mill.

10 The very first test to check the pigment dispersion is to look on the grinding gauge. The pigment paste is drawn down the slot with reducing depth. The depth of the slot usually varies from 25 to 1 micron (sensitivity being ± 1 micron). Undispersed pigment particles in the form of agglomerates stick out of the film when the paste is drawn down giving scratches. Up to 3 scratches at 5 micron is acceptable, as it is practically not
15 possible to disperse all the pigments (100%).

Once the pigment has achieved this fineness, the pigment paste is diluted with the letdown. The finished ink is then printed onto polypropylene films using the flexo proofer. This proofer gives an uniform film of around 1 micron thickness. The ink film is then cured under a UV lamp (120W/cm at 30 m/min). The compositions prepared are given in
20 Table 1, where the figures are in weight %

Table 1

	INK COMPOSITION				PIGMENT PASTE			
	Cyan	Magenta	Yellow	Black	Cyan	Magenta	Yellow	Black
Monomer	24	24.6	26.56	21.6	60	61.5	66.4	54
Irgalite GLO	14				35			
Ilobona 4BY203		14				35		
Irgalite BAW			12				30	
Special Black 250				16				40
Solsperse 24000 SC	1.2	1	0.8	2	3	2.5	2	5
Solsperse 22000	0.4				1			
Solsperse 5000				0			0.6	
Stabilizer	0.4	0.4	0.4	0.4	1	1	1	1
Photoinitiator	9.5	9.5	9.5	9.5				
Ebecryl 40 *	50	50	50	50				
Silicone oil PA 57	0.5	0.5	0.5	0.5				

* Ebecryl 40 is the tradename of tetracrylated alkoxylated pentacrythritol sold by UCB, S.A.

Example 2

The cured ink on the film is then observed against a light source to detect any 5 haziness or evaluate its transparency. The better the quality of dispersion, the better the transparency. The colour strength was looked at both visually with the naked eye in examples 2 and 3 and in the diluted inks of examples 5 and 7 and with a densitometer "Spectro Eye" of GRETAG for the concentrated inks of examples 5 and 7. Sometimes the strength of the ink is very high and it is not easy to notice minor differences in 10 transparency and density. The higher the colour strength, the higher the density. Hence the inks are further diluted with a diluting medium (usually a diacrylate monomer and some photoinitiator) in the ratio 10% ink to 90% diluent. The diluted ink is then applied with a laboratory coater manually. A film of about 10 microns is printed and cured again under the UV light. The film is once again observed for its transparency and colour 15 strength. The flow of the liquid ink is rated as A if the flows freely or after a small shock. The purity is evaluated with a printed sample on plastic film. Flocculation, light scattering, bronzing or undertones were taken into account. The results are given in Table 2 and Table 2A.

In these tables, "trans" stands for "transparency".

20 In the following tables, the values of the properties are relative to TCDA for which the value of "0" has been given for that property. Values of minus are given when the property is worse than that of TCDA and values of plus are given when the property is better than that of TDCA.

Following abbreviations are used in the tables:

25 EO : ethoxylated
PO : propoxylated
PEG : polyethyleneglycol
NPG : neopentylglycol
TMP : trimethylolpropane
30 di-TMPTA : ditrimethylolpropane tetraacrylate
Ph : phenyl
DPGDA : dipropyleneglycol diacrylate

Table 2

PIGMENT WETTING OF LIQUID RESINS AND MONOMERS IN PRESENCE OF DISPERSING ADDITIVE

COMPOSITIONS	YELLOW						MAGENTA					
	Conc. Ink			90% diluted ink			Conc. Ink			90% diluted Ink		
	trans	Flow	gloss	trans	strength	purity	trans	Flow	Gloss	trans	strength	purity
Isobornyl acrylate	--	A	+	0	0	0	0	A	---	0	-	--
Octyl/decyl acrylate	-	A	0	-	0	0	0	A	---	---	---	---
N-Vinyl pyrrolidone	---	A	--	---	---	---	--	A	---	---	---	---
4-t-Butyl cyclohexanol acrylate	--	A	+	0	0	0	--	A	-	-	+	--
Phenyl (EO) ₁ acrylate	--	A	+	-	0	0	0	A	0	-	+	--
Phenyl (EO) ₂ acrylate	--	A	--	0	-	0	0	A	0	0	-	--
Ethoxycethoxyethyl acrylate	--	A	--	0	-	0	0	A	0	0	-	--
Tricyclodecyl monoacrylate	-	A	0	0	0	-	0	A	-	+	+	+
Tricyclodecyl diacrylate	0	A	0	0	0	0	0	A	0	0	0	0
Dipropylene glycol diacrylate	--	A	--	+	0	0	+	A	0	0	0	0
Tripropylene glycol diacrylate	--	A	0	0	+	0	0	A	0	0	0	0
Hexanediol diacrylate	--	A	+	-	--	0	+	A	0	0	0	0
Tetraethylenglycol diacrylate	--	A	--	0	+	0	0	A	0	0	0	0
PEG 600 diacrylate	--	A	--	-	0	0	--	A	---	---	---	---
NPG (OP) ₂ diacrylate	0	A	-	0	0	0	--	A	---	---	0	--
Trimethylene propane triacrylate	-	A	-	0	+	0	--	A	---	---	---	---
TMP (EO) ₃ triacrylate	0	A	--	0	0	0	+	A	0	0	0	0
TMP (EO) ₁₅ triacrylate	--	A	--	-	-	0	--	A	---	---	---	---
Glycerol(OP) ₃ triacrylate	--	A	--	+	0	0	+	A	--	---	---	---
Pentaerythritol triacrylate	-	A	--	+	0	0	0	A	0	0	0	0
di-TMPFA	0	A	-	0	--	0	--	A	---	-	-	-

Table 2A

PIGMENT WETTING OF LIQUID RESINS AND MONOMERS IN PRESENCE OF DISPERSING ADDITIVE

COMPOSITIONS	CYAN						BLACK					
	Conc. Ink		90% diluted ink		Conc. Ink		90% diluted Ink		Trans		strength	
Trans	Flow	gloss	Trans	Strength	Purity	Trans	Flow	Gloss	Trans	strength		Purity
Isobornyl acrylate	-	A	--	--	0	--	A	--	-	-	0	0
Octyl/decyl acrylate	--	A	-----	0	0	--	A	---	--	--	0	0
N-Vinyl pyrrolidone	-	A	0	--	0	0	-	A	---	---	0	0
4-tButyl cyclohexanol acrylate	0	A	0	---	0	0	-	A	--	-	++	0
Phen(EO) ₁ acrylate	--	A	0	0	0	-	A	--	+	+	++	0
Phen (EO) ₂ acrylate	0	A	0	---	0	--	A	--	-	-	0	0
Ethoxyethoxyethyl acrylate	---	A	-----	--	0	--	A	---	--	0	0	0
Tricyclodecyl monoacrylate	0	A	0	0	0	+	A	0	0	-	-	-
Tricyclodecyl diacrylate	0	A	0	0	0	0	A	0	0	0	0	0
Dipropylene glycol diacrylate	0	A	0	--	---	--	A	--	-	0	0	0
Tripropylene glycol diacrylate	0	A	0	--	---	--	A	--	-	0	0	0
Hexanediol diacrylate	0	A	----	----	----	--	A	--	-	+	+	0
Tetraethylenglycol diacrylate	--	A	--	----	----	--	A	--	----	--	-	-
PEG 600 diacrylate	----	A	-----	-----	-----	-----	A	-----	-----	-----	-----	-----
NPG (OP) ₂ diacrylate	-	A	--	--	0	+	A	0	-	0	0	0
Trimethylene propane triacrylate	0	A	--	--	0	--	A	--	-	0	0	0
TMP (EO) ₃ triacrylate	0	A	----	--	---	--	A	--	-	-	+	0
TMP (EO) ₁₅ triacrylate	----	A	-----	-----	-----	-----	A	-----	-----	0	0	0
Glycerol(OP) ₃ triacrylate	0	A	--	--	---	--	0	A	--	-	0	0
Pentaerythritol triacrylate	-	A	--	-	---	0	-	A	--	-	+	0
di-TMFTA	-	A	-	0	--	0	--	A	--	-	0	0

Binders that are not good for dispersion do not show a transparent film on printing. The film usually is hazy with a lot of fine particles sticking to each other. In worst cases the pigment flocculate to each other and the printed film looks almost clear with hardly any colour.

5 Example 3

We also observed the printed films of the concentrated inks under the microscope under 25x magnification. It is possible to see the quality of dispersion. Bad dispersion in the form of agglomerates or flocculation of pigment particles can be seen. Based on all the 10 above observations a rating is given for gloss, transparency and strength. Results are given in Table 3.

Table 3

Microscope evaluation										
Description	YELLOW			MAGENTA			CYAN			BLACK
	Quality	Remarks	Concentrated ink	Quality	Remarks	Concentrated ink	Quality	Remarks	Concentrated ink	
Isobornyl acrylate	0	Almost as good	0/+	Same, no air	-	Agglomerates	Small	-	Concentrated ink	Concentrated ink
Octyl/decyl acrylate	-	Flocculation + Agglom.	-	Slight Flocculation	-	Agglomerates	Slight	---	Concentrated ink	Concentrated ink
N-vinyl pyrrolidone	---	Completely Floculated	-	Flocculation	0/-	Flocculation	Very Slight	---	Flocculation	Flocculation
4 tButyl cyclohexanol acrylate	-	Slight Flocculation	-	Slight Flocculation	++	Flocculation	Better	-	Matt, small agglomerates	Matt, small agglomerates
Phenyl(OE) ₁ acrylate	-	Very slight Flocculation	++	Better	++	Better	Better, no air	-	Small aggl. air entrap	Small aggl. air entrap
Phenyl(OE) ₂ acrylate	-	Flocculation	++	Better, no air	0/+	No air	No air	-	Matt	Matt
Ethoxyethoxyethyl acrylate	-	Flocculation	+	No Air	-	Flocculation	---	---	Small agglomerates	Small agglomerates
Tricyclodecyl diacrylate	0	Almost as good	0	same, less air	0	Better, no air	0	As good	Slight	Flocculation
Dipropylene glycol diacrylate	0/-	Slight Flocculation	++	Better, no air	+	Better	Better	---	Small agglomerates	Small agglomerates
Tripropylene glycol diacrylate	-	Flocculation + Agglom.	+	No air	++	Better, no air	-	As good	Small agglomerates	Small agglomerates
Hexanediol diacrylate	-	Flocculation	0/+	No air	0/+	No air	-	Small	-	-
Tetraethylenglycol diacrylate	-	Flocculation	0	No air, agglomerates	+	Better	-	Small	agglomerates	agglomerates
PEG 600 DA	--	Floculated	--	Flocculation	--	Flocculation	---	Small	Flocculation	Flocculation
NPG(OP) ₂ DA	0/-	Very slight Flocculation	-	Small Agglomerates	+	Better	0/-	Small	agglomerates	agglomerates
Trimethylolpropane triacrylate	-	Flocculation + Agglom.	0/-	Small Agglomerates	-	Air Entrapped, agglomer	-	-	-	-
TMP(EO) triacrylate	-	Slight Flocculation	++	Better	+	Better, no air	-	-	-	-

TMP(EO) ₁₅ triacrylate	-	Slight Flocculation	-	Flocculation + Agglom	-	Flocculation	-	Small agglomerates
Glycerol(OP) ₃ triacrylate	-	Slight Flocculation	++	Better, no air	0/+	No air	0/-	Small agglomerates
Pentaerythritol triacrylate	-	Slight Flocculation	+	Better, no air	++	Better, no air	--	-
di TMPTA	0/-	Small agglomerates	0	Agglomerates	0	No air	-	-

From Tables 2, 2A and 3, it can be seen that TCDA shows the best pigment wetting results from the monomers when all colors are taken into consideration. Some monomers give better or equal pigment wetting for one color or exceptionally for two colors but never for the entire series. When other aspects like odor and reactivity are taken into consideration, TCDA comes out as the best choice for ink jet inks.

5

Example 4

This example describes the rheology of the inks in terms of viscosity in function of shear rate. TCDA is giving the lowest shortness index (SI) and hence the best Newtonian behaviour, as required for liquid inks.

10

Table 4

Rheology of the inks			
BINDERS	CYAN		
	Visc. 2,5 (1/s) (mPa.s)	Visc. 100 (1/s) (mPa.s)	Shortness index
Phenyl(OE) ₁ acrylate	1000	325	3.08
	1410	358	3.94
	708	500	1.42
	1190	267	4.46
	445	218	2.04
	2200	444	4.95
MAGENTA			
Phenyl(OE) ₂ acrylate	2707	328	8.25
	3335	387	8.62
	3601	701	5.14
	3446	337	10.23
	2323	277	8.39
	3369	572	5.89

15

Example 5

Tests were also done for TCDA, DPGDA and phenoxyethyl acrylate with different pigments (Cyan, Magenta, Yellow and Black) in order to prove the general applicability of the results, which are given in Table 5. The composition of the inks corresponds to the one given in example 1 with exception of the pigment. For cyan, Irgalite GLO was replaced by Hostaperm Blue B2G. For magenta Illobona 4BY was replaced by Irgalite SMA. For yellow Irgalite BAW was replaced by Permanent GR. For black Special Black 250 was replaced by Special Black 350.

Table 5

YELLOW (Permanent GR)							MAGENTA (Irgalite magenta SMA)						
conc. ink				90% diluted ink			conc. ink				90% diluted ink		
Trans.	gloss	strength	S.I.	Trans.	strength	Trans.	Gloss	strength	S.I.	Trans.	strength		
TCDA	0	1,41	29,5	0	0	0	0	1,40	15,5	0	0	0	0
DPGDA	0	1,28	42,5	0	-	0	0	1,49	17,1	-	-	-	-
Phenyl(OE) ₁ acrylate	0	1,35	39,6	-	0	0	0	1,40	23,2	-	-	-	-
BLACK (Special Black 350)							CYAN (Hostapern Blue B2G)						
conc. ink				90% diluted ink			conc. ink				90% diluted ink		
Trans.	gloss	strength	S.I.	Trans.	strength	Trans.	Gloss	strength	S.I.	Trans.	strength		
TCDA	0	2,13	4,5	0	0	0	0	2,09	3,0	0	0	0	0
DPGDA	-	2,10	8,4	--	--	--	0	2,03	10,7	-	-	-	-
Phenyl(OE) ₁ acrylate	-	2,18	10,5	0	-	-	0	2,18	4,8	0	0	-	-

S.I. = shortness index

Also with these four pigments, TCDA is the better pigment wetter as shown by the better gloss, transparency, color strength and the lower shortness index (more Newtonian character).

Example 6

The general applicability of the results can also be seen in the rheology of the inks based on TCDA, DPGDA and phenoxyethyl acrylate with different pigments. In all cases TCDA is showing the lowest shortness index (SI).

Shear Rate / Visc. (mPa.s)	YELLOW (Permanent GR)			MAGENTA (Irgalite SMA)		
	TCDA	DPGDA	Ph(OE) ₁ acrylate	TCDA	DPGDA	Ph(OE) ₁ acrylate
2,72 s ⁻¹	18300	15300	16600	6990	4290	6410
13,00 s ⁻¹	4580	3590	3950	1640	953	1260
26,00 s ⁻¹	2640	1940	2170	1080	624	781
62,10 s ⁻¹	1430	961	1080	784	449	519
105,0 s ⁻¹	1040	669	758	658	373	422
250,0 s ⁻¹	673	398	456	491	276	304
500,0 s ⁻¹	504	285	324	402	223	243
S.I. (2,5/250)	29.5	42.5	39.6	15.5	17.1	23.2
BLACK (Special Black 350)						
Shear Rate / Visc. (mPa.s)	TCDA			CYAN (Hostaperm Blue B2G)		
	TCDA	DPGDA	Ph(OE) ₁ acrylate	TCDA	DPGDA	Ph(OE) ₁ acrylate
2,72 s ⁻¹	1920	2140	2930	1030	2690	1180
13,00 s ⁻¹	1220	957	1150	671	1000	574
26,00 s ⁻¹	915	656	766	585	698	461
62,10 s ⁻¹	660	437	496	493	468	370
105,0 s ⁻¹	556	355	397	435	375	325
250,0 s ⁻¹	437	262	289	350	270	260
500,0 s ⁻¹	372.0	214.0	234.0	299	216	218
S.I. (2,5/250)	4.5	8.4	10.5	3.0	10.7	4.8

Example 7

A couple of inks were also made without dispersing additives. Again the four process colors (Cyan, Magenta, Yellow and Black) were used. TCDA was compared to DPGDA

		YELLOW				
		conc. ink			90% diluted ink	
		Trans.	gloss	strength	Trans.	strength
TCDA		+	+	1,39	0	0
DPGDA		++	+	1,33	+	+
		CYAN				
		conc. ink			90% diluted ink	
		Trans.	gloss	strength	Trans.	strength
TCDA		0	0	1,63	0	0
DPGDA		--	--	1,47	---	---
		MAGENTA				
		conc. ink			90% diluted ink	
		Trans..	gloss	strength	Trans.	strength
TCDA		0	0	1,27	0	0
DPGDA		---	---	1,17	--	--
		BLACK				
		conc. ink			90% diluted ink	
		Trans.	gloss	strength	Trans.	strength
TCDA		0	0	1,36	0	0
DPGDA		-----	---	1,08	---	-----

5

Conclusion: TCDA performed better than DPGDA in terms of transparency, gloss and color strength.

Claims

1. Radiation curable liquid ink composition having a viscosity (measured at a temperature of 25°C and at a shear rate of 500 s⁻¹) of at most 1000 mPa.s, such 5 composition containing tricyclodecyl di(meth)acrylate and/or tricyclodecyl mono(meth)acrylate and a pigment.
2. Radiation curable liquid ink composition according to claim 1, characterised in that it comprises:
 - (a) 1-85% by weight of tricyclodecyl di(meth)acrylate and/or tricyclodecyl 10 mono(meth)acrylate;
 - (b) 1-50% by weight of a pigment;
 - (c) 0-85% by weight of an acrylic and/or methacrylic derivative;
 - (d) 0-15% by weight of a photoinitiator;
 - (e) 0-15% by weight of a dispersing agent;
 - (f) 0-10% by weight of additives,
- 15 calculated on the total weight of the composition.
3. Radiation curable liquid ink according to any of claims 1 or 2, wherein the (meth)acrylic derivative (c) is a monomer or an oligomer, used alone or in admixture.
4. Radiation curable liquid ink according to any of claims 1 to 3 used as ink jet ink.
- 20 5. Radiation curable liquid ink according to any of claims 1 to 4 used in flexography printing.
6. Radiation curable liquid ink according to any of claims 1 to 5 used in gravure printing.
7. Radiation curable liquid ink according to any of claims 1 to 6, wherein the radiation 25 curing is performed by one or more ultraviolet and/or electron beam sources.
8. Polymeric composition obtained or obtainable by curing the radiation curable liquid ink composition according to any preceding claim.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/14544

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C09D11/10 C08F222/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C09D C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

WPI Data, EPO-Internal, PAU

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 199706 Derwent Publications Ltd., London, GB; Class A12, AN 1997-061832 XP002198135 & JP 08 311130 A (TOSHIBA CHEM CORP), 26 November 1996 (1996-11-26) cited in the application abstract</p> <p>—</p> <p>—/—</p>	1-3, 7

Further documents are listed in the continuation of box C.

Patent family members are listed in annex.

* Special categories of cited documents :

- *'A' document defining the general state of the art which is not considered to be of particular relevance
- *'E' earlier document but published on or after the international filing date
- *'L' document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *'O' document referring to an oral disclosure, use, exhibition or other means
- *'P' document published prior to the international filing date but later than the priority date claimed

- *'T' later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *'X' document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *'Y' document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *'G' document member of the same patent family

Date of the actual completion of the international search

24 April 2003

Date of mailing of the International search report

06/05/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Matthijssen, J-J

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP 02/14544

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT	
Category	Relevant to claim No.
X	<p>DATABASE WPI Section Ch, Week 198246 Derwent Publications Ltd., London, GB; Class A97, AN 1982-98516E XP002198136 & JP 57 164163 A (TOYO INK MFG CO), 8 October 1982 (1982-10-08) cited in the application abstract</p> <p>---</p>
A	<p>EP 0 540 203 A (DOMINO PRINTING SCIENCES PLC) 5 May 1993 (1993-05-05) cited in the application column 2, line 18 - line 25 column 2, line 35 - line 42 column 3, line 35 -column 4, line 14 column 4, line 45 - line 52</p> <p>---</p>
X	<p>WO 99 48928 A (DAINIPPON INK & CHEMICALS ;SAKURAI YOSHINOBU (JP); TAKAHASHI KATSU) 30 September 1999 (1999-09-30) page 31, line 30 -page 32, line 17 page 41, line 14 - line 32 page 43, line 10 - line 15 page 45, line 20 - line 36</p> <p>---</p>

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/14544

Patent document cited in search report		Publication date		Patent family member(s)		Publication date
JP 8311130	A	26-11-1996	NONE			
JP 57164163	A	08-10-1982	JP JP	1759621 C 3053344 B	20-05-1993 14-08-1991	
EP 0540203	A	05-05-1993	DE DE EP JP US	69215835 D1 69215835 T2 0540203 A1 5214280 A 5275646 A	23-01-1997 03-04-1997 05-05-1993 24-08-1993 04-01-1994	
WO 9948928	A	30-09-1999	JP JP JP JP AU EP EP JP US WO	11124403 A 11124404 A 11292874 A 11302278 A 1586499 A 0878482 A1 1073685 A1 2003508546 T 6410611 B1 9948928 A1	11-05-1999 11-05-1999 26-10-1999 02-11-1999 18-10-1999 18-11-1998 07-02-2001 04-03-2003 25-06-2002 30-09-1999	

Form PCT/ISA/210 (patent family annex) (July 1992)